

FILE HISTORY OF PROVISIONAL APPLICATION S/N 60/439,288

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PROVISIONAL APPLICATION FOR PATENT COVER SHEET

This is a request for filing a PROVISIONAL APPLICATION FOR PATENT under 37 CFR 1.53(c).

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<input checked="" type="checkbox"/> Additional inventors are being named on the <u>1</u> separately numbered sheets attached hereto			
TITLE OF THE INVENTION (280 characters max) COATINGS, MATERIALS, ARTICLES, AND METHODS OF MAKING THEREOF			
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ENCLOSED APPLICATION PARTS (check all that apply)			
<input checked="" type="checkbox"/> Specification	Number of Pages <u>24</u>	<input type="checkbox"/> CD(s), Number	
<input checked="" type="checkbox"/> Drawing(s)	Number of Sheets <u>10</u>	<input type="checkbox"/> Other (specify)	
<input type="checkbox"/> Application Data Sheet. See 37 CFR 1.78			
METHOD OF PAYMENT OF FILING FEES FOR THIS PROVISIONAL APPLICATION FOR PATENT (check one)			
<input checked="" type="checkbox"/> Applicant claims small entity status. See 37 CFR 1.27.		FILING FEE AMOUNT (\$)	
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<input checked="" type="checkbox"/> The Commissioner is hereby authorized to charge filing fees or credit any overpayment to Deposit Account Number <u>06-1130</u>		\$80.00	
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The invention was made by an agency of the United States Government or under a contract with an agency of the United States Government.			
<input type="checkbox"/> No.			
<input checked="" type="checkbox"/> Yes, the name of the U.S. Government agency and the Government contract number are: <u>Office of Naval Research</u> <u>grant numbers N00014-98-C-0010, N00014-02-1-0171.</u>			

Respectfully submitted,

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1/10/03

REGISTRATION NO.

48,137

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Docket Number:

UCT-0040

USE ONLY FOR FILING A PROVISIONAL APPLICATION FOR PATENT

This collection of information is required by 37 CFR 1.51. The information is used by the public to file (and by the PTO to process) a provisional application. Confidentiality is governed by 35 U.S.C. 122 and 37 CFR 1.14. This collection is estimated to take 8 hours to complete, including gathering, preparing, and submitting the complete provisional application to the PTO. Time will vary depending upon the individual case. Any comments on the amount of time you require to complete this form and/or suggestions for reducing this burden, should be sent to the Chief Information Officer, U.S. Patent and Trademark Office, U.S. Department of Commerce, Washington, D.C. 20231. DO NOT SEND FEES OR COMPLETED FORMS TO THIS ADDRESS. SEND TO: Box Provisional Application, Assistant Commissioner for Patents, Washington, D.C.

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PROVISIONAL APPLICATION COVER SHEET
Additional Page

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Docket Number		UCT-0040		Type s plus sign (+) inside this box → +
INVENTOR(S)/APPLICANT(S)				
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CERTIFICATE OF MAILING BY "EXPRESS MAIL" (37 CFR 1.10) Applicant(s): Gell, et al.			Docket No. UCT-0040
Serial No.	Filing Date	Examiner	Group Art Unit
Invention: COATINGS, MATERIALS, ARTICLES, AND METHODS OF MAKING THEREOF			
<p>I hereby certify that the following correspondence:</p> <div style="border: 1px solid black; padding: 10px; margin: 10px 0;"> Provisional Application Cover Sheet, Provisional Application, 10 Sheets of formal drawings; Check in the amount of \$80.00 and Postcard </div> <p style="text-align: center;"><i>(Identify type of correspondence)</i></p> <p>is being deposited with the United States Postal Service "Express Mail Post Office to Addressee" service under 37 CFR 1.10 in an envelope addressed to: The Assistant Commissioner for Patents, Washington, D.C. 20231 on</p> <p style="text-align: center;"> <u>January 10, 2003</u> <i>(Date)</i> </p> <div style="text-align: right; margin-top: 20px;"> <p>Tracy A. Sweatt</p> <p><i>(Typed or Printed Name of Person Mailing Correspondence)</i></p> <hr style="border: 0; border-top: 1px solid black; margin: 5px 0;"/> <p><i>(Signature of Person Mailing Correspondence)</i></p> <hr style="border: 0; border-top: 1px solid black; margin: 5px 0;"/> <p>EV 052918052 US</p> <p><i>(“Express Mail” Mailing Label Number)</i></p> </div>			
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COATINGS, MATERIALS, ARTICLES, AND METHODS OF MAKING
THEREOF

STATEMENT REGARDING FEDERALLY SPONSORED RESEARCH &
DEVELOPMENT

The U.S. Government has certain rights in this invention pursuant to Office of
5 Naval Research grant numbers N00014-98-C-0010, N00014-02-1-0171.

BACKGROUND

There is a wide variety of methods for forming a coating or deposited material.
Methods include chemical vapor deposition, laser assisted pyrolysis deposition,
electron-beam physical vapor deposition and thermal spray. The material produced by
10 these methods can vary significantly in microstructure from method to method. The
microstructure of the material, as well as its composition, has a significant impact on
the end use of the material. Thus it is clear that there is a complex interaction between
the microstructure of the material, the composition of the material, the end use of the
material and the method of making the material.

15 Microstructure, as used herein, refers to the structure of the material or coating
on a microscopic level. Components of microstructure include the phases present,
grain size, precipitate and dispersoid size, density/porosity, cracking, and the presence
and size of lamellar splats (in thermal spray methods). Splats are the result of molten
or partially molten particles impinging upon a substrate at a high temperature, high
20 speed or combination of high temperature and high speed. The size of the splat
boundary is related to the size of the splat and large splat boundaries may result in
lateral cracking, potentially causing material failure. These components of
microstructure may affect gross physical properties of the coating such as thermal
conductivity, bond strength, elastic modulus and so forth. As can be readily
25 appreciated some of these gross physical characteristics are desirable in some uses and
not in others. None of the currently available methods of deposition is capable of
manipulating all the above-described microstructural features.

Of the above-described methods, thermal spray is the most flexible with regard to feedstocks. Thermal spray may employ a solid, powdered feedstock, a dispersion of a solid, powdered feedstock in a liquid carrier, or a liquid precursor. Thermal spray is highly flexible with regard to the composition of the feedstock owing to the variety of flame types, velocities and flame temperatures available in thermal spray techniques resulting in a wide compositional variety in the produced materials. Additionally, thermal spray generally is highly efficient making it a cost effective method.

What is needed in the art is a cost effective method of material deposition that can produce materials and coatings with a variety of compositions and microstructural features.

BRIEF SUMMARY

The above-described and other drawbacks are alleviated by a method of producing a material comprising injecting precursor solution droplets into a hot zone of a thermal spray flame, converting the precursor solution droplets into particles, at least partially melting the particles and depositing the particles on a substrate. The substrate may be optionally preheated and/or maintained at a desired temperature during material deposition. The material produced by this method comprises splats having an average diameter of less than or equal to about 2 micrometers. Additionally the splats preferably have a thickness less than or equal to about 800 nanometers. The material also exhibits three dimensional porosity of about 1 to about 50 volume percent, and the pores may be micrometer sized (about 0.5 to about 10 micrometers), nanometer sized (up to about 100 nanometers) or a combination of micrometer and nanometer sized pores. The material can optionally have vertical cracks that vary in length from about 0.8 to 1.0 times the thickness of the material. The vertical cracks generally are spaced at a distance less than the coating thickness but can be spaced at distances up to two times the thickness of the material. The material may be employed as a coating over a large thickness range of about 2 micrometers to over 3 millimeters or as a structural preform.

BRIEF DESCRIPTION OF THE DRAWINGS

Referring now to the drawings wherein like elements are numbered alike in several FIGURES:

Figure 1 is a schematic diagram of a solution plasma spray system.

- 5 Figure 2 shows graphs of the effects of varying process parameters on the spacing of vertical cracks (A) and the coating density (B).

Figure 3 shows a schematic illustration of a solution plasma spray-deposited coating (C) in comparison to those formed in the electron beam physical vapor deposition process and (A) and conventional thermal spraying (B).

- 10 Figure 4 shows scanning electron micrographs (SEM) of cross-sections of a solution plasma spray-deposited coating of zirconia stabilized with 7 weight percent yttria based on the total weight of the material (7YSZ).

Figure 5 shows a schematic of the microstructure of a solution plasma spray-deposited 7YSZ coating.

- 15 Figure 6 shows SEM fracture morphologies of solution plasma spray-deposited zirconia stabilized with 20 weight percent yttria (20YSZ) coatings at two different magnifications.

- Figure 7 shows SEM microstructural observations of a low-porosity 20YSZ coating (A) and a high-porosity lanthia-doped ceria (LDC) + nickel oxide (NiO) coating (B) deposited by the solution plasma spray process.
- 20

Figure 8 shows a thick 7YSZ coating on a superalloy substrate.

Figure 9 shows the durability of a solution plasma spray-deposited 7YSZ thermal barrier coating in a thermal cycle test.

- 25 Figure 10 shows the thermal cycling behavior of a solution plasma spray-deposited 7YSZ coating compared to control air plasma sprayed coating as a function of the coating thickness.

Figure 11 shows the thermal cycling behavior of a solution plasma spray-deposited 7YSZ coating compared to control air plasma sprayed coatings as a function of the substrate roughness.

- Figure 12 shows the thermal conductivity of a solution plasma spray-deposited 7YSZ thermal barrier coating compared to a conventional thermal sprayed coating and an electron beam plasma vapor deposited coating.

Figure 13 shows the performance of a 20YSZ coating applied using the solution plasma spray method bent at angle of 90°.

- Figure 14 shows the X-ray diffraction pattern for an LDC+NiO anode layer deposited by the solution plasma spray process.

Figure 15 shows the cross-section microstructure of solution plasma spray-formed LDC and LDC+NiO layers in a solid oxide fuel cell (SOFC).

Figure 16 shows the microstructure of solution plasma spray-deposited coating.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

- A method of producing a material comprises injecting precursor solution droplets into a hot zone of a thermal spray flame, converting the precursor solution droplets into particles, at least partially melting the particles and depositing the particles on a substrate. The substrate may be optionally preheated and/or maintained at a desired temperature during material deposition. The material produced by this method comprises splats having an average diameter of less than or equal to about 2 micrometers. Additionally the splats preferably have a thickness less than or equal to about 800 nanometers. All splats in the material are less than about 5 micrometers in diameter. The material also exhibits of about 1 to about 50 volume percent, and the pores may be micrometer sized (about 0.5 to about 10 micrometers), nanometer sized (up to about 100 nanometers) or a combination of micrometer and nanometer sized pores. The material can optionally have vertical cracks that vary in length from about 0.8 to 1.0 times the thickness of the material. The vertical cracks generally are spaced

at a distance less than the coating thickness but can be spaced at distances up to two times the thickness of the material. The material may be employed as a coating over a large thickness range (about 2 micrometers to over 3 millimeters) or as a structural preform.

- 5 It has been unexpectedly discovered that injecting the precursor solution droplets into the hot zone of the flame results in a material having an average splat size less than or equal to about 2 micrometers. The droplets need sufficient mass and velocity to carry the droplets into the hot zone. Without being bound by theory it is believed that upon entering the hot zone of the flame the droplets have formed or
- 10 rapidly form a crust. As the solvent portion of the droplet inside the crust vaporizes the droplet explodes resulting in the formation of a large number of very small droplets and/or particles. As can be readily appreciated based on this theory parameters such as precursor solution viscosity, precursor solution surface tension, precursor solution concentration and droplet residence time in the flame and
- 15 particularly in the hot zone of the flame may have bearing on the splat size. Moreover, coating deposition efficiency is enhanced relative to other solution injection methods.

- Additionally it has been discovered that heating the substrate prior to thermal spraying and/or maintaining the substrate temperature within a desired range can
- 20 impact the bond strength and microstructure of the materials produced, particularly in the formation of coatings such as thermal barrier coatings.

- Useful substrates include, but are not limited to, metals, coated metals such as bond coated metals, ceramics, cermets, and plastics. The substrate must be capable of withstanding the conditions of the thermal spray process. For example, when the
- 25 thermal spray process includes preheating the substrate, the substrate material should be capable of being heated to the desired preheat temperature without structural degradation. Exemplary materials capable of withstanding preheating include, but are not limited to, stainless steel, titanium, aluminum, superalloys and ceramics. In contrast to currently available thermal spray methods, in one embodiment the surface
- 30 roughness of the substrate has little or no impact on the material-substrate bond

strength. The thermal spray method described herein is capable of forming a material on a polished substrate and the resulting composite material exhibits excellent bond strength as demonstrated by substantially no delamination or spalling.

The substrate may be preheated, typically by employing a temperature control unit. The temperature control unit may comprise a heat supply, a cooling jet, temperature measurement means and optionally temperature recording means. The temperature measurement means is located on the substrate side opposite the thermal spray flame source for reliability and durability. The heat supply may be, for example, a scanning thermal spray flame, an electrical resistance heater or other heating device known in the art. Preheat temperatures are greater than room temperature, preferably greater than or equal to about 150°C, and more preferably greater than or equal to about 200°C. Additionally the preheat temperature is typically less than or equal to about 600°C, preferably less than or equal to about 500°C, and more preferably less than or equal to about 400°C. Alternatively or in addition the temperature control unit may be used to maintain the substrate and/or deposited material at a desired temperature range during thermal spray. Typically the desired temperature of the substrate and/or deposited material during thermal spray is greater than or equal to about 250°C, preferably greater than or equal to about 275°C, and more preferably greater than or equal to about 300°C. It is envisioned that the maximum desired temperature for the substrate and/or deposited material during solution thermal spray would be less than or equal to about 700°C, preferably less than or equal to about 650°C, and more preferably less than or equal to about 600°C.

The precursor solution may be prepared by dissolving a precursor in a solvent. The precursor may be a liquid or a solid such as a precursor salt. Suitable precursor salts comprise, for example, carboxylate salts, acetate salts, nitrate salts, chloride salts, alkoxide salts, butoxide salts, and the like of, for example, alkali metals, alkaline earth metals, transition metals, rare earth metals and the like, and combinations comprising one or more of the foregoing salts. Preferred precursor salts include, for example, zirconium acetate, yttrium nitrate, aluminum nitrate, nickel nitrate, cerium acetate, lanthanum acetate, iron nitrate, zinc nitrate, and combinations comprising one or more of the foregoing salts.

Suitable solvents include those solvents and combinations of solvents capable of dissolving the precursor(s). Exemplary solvents include water, alcohols having 1 to about 5 carbons, carboxylic acids, organic solvents, and combinations of the foregoing solvents.

- 5 In the case of complex compounds such as a mixed oxide ceramic, the reagents are weighed according to the desired stoichiometry of the final compound, i.e., mixed oxide, and then added and mixed with the solution. The precursor solution may be heated and stirred to dissolve the solid components and homogenize the solution. Reagent grade precursors may be suitable for the manufacture of the
- 10 coatings, particularly for doped semiconductors or oxide membranes used as electronic components, electrodes or electrolytes. Industrial grade precursors may be preferred for the manufacture of structural thick coatings or bulk materials due to the low cost of the starting chemicals. For the fabrication of composite or graded coatings, two or more different precursor solutions may be prepared, and stored in
- 15 individual containers. The precursor solutions may then be combined prior to spraying or atomized in separate nozzles and sprayed simultaneously or sequentially.

- The precursor solution is delivered to an atomizing injector nozzle. In a preferred embodiment the precursor solution is atomized into micrometer sized droplets in the atomizing injector nozzle and injected into the thermal spray flame
- 20 radially. The precursor solution may be injected into the thermal spray flame coaxially. When the precursor solution is injected radially, the injector nozzle may be oriented at an angle of about 45° to about 90° relative to the axis of the flame. Preferably the injector nozzle is oriented at about 90° relative to the flame axis. The injection position may impact the porosity of the deposited material and the presence
- 25 or absence of vertical cracks. Multiple injectors may be used forming composite or graded materials or increasing deposition efficiency.

- Micrometer sized droplets are herein defined as having a diameter less than or equal to about 50 micrometers, preferably less than or equal to about 300 micrometers and more preferably less than or equal to about 20 micrometers. Additionally,
- 30 micrometer sized droplets have a diameter greater than or equal to about 0.5

micrometers, preferably greater than or equal to about 0.75 micrometers, and most preferably greater than or equal to about 1 micrometer. Preferably the atomizing gas used in the injector nozzle typically has a pressure within about 15%, preferably within about 10% and more preferably within about 5% of the precursor solution.

- 5 Useful thermal spray methods include all known types of thermal spray. Preferably plasma spray is employed. When plasma spray is the thermal spray method, the porosity and the generation of vertical cracks can be impacted by the argon flowrate. In the case of porosity, a low degree of porosity may be produced using a low argon flow rate. The lower argon flow rate results in a higher temperature
- 10 plasma flame. In the case of vertical cracking, a high argon flow rate may reduce the spacing between the vertical cracks. The high argon flow rate results in a lower temperature flame. Parameters of other types of thermal spray may be similarly modified to achieve similar effects.

- The material formed by the solution plasma spray process has fine splats. A
- 15 splat is defined as a thin platelet formed when the material formed in the plasma flame from the precursor solution droplets impinges on the substrate. Splats may typically be described as having a length, width and thickness. For convenience, the diameter is herein defined as the length or the width, whichever is greater. Fine splats are defined as having an average diameter less than about 2 micrometers, preferably less
- 20 than or equal to about 1.5 micrometers, and more preferably less than or equal to about 1 micrometer in size. Additionally the splats have a thickness less than or equal to about 800 nanometers, preferably less than or equal to about 700 nanometers, and more preferably less than or equal to about 600 nanometers.

- The material typically exhibits porosity of about 1 to about 50 volume percent,
- 25 based on the total volume of the material. The porosity is three-dimensional when the porosity is greater than or equal to about 8%. Three-dimensional porosity is herein defined as interpenetrating porosity substantially evenly and randomly distributed throughout the material. The pores may be micrometer sized (to about 10 micrometers), nanometer sized (up to about 100 nanometers) or preferably a
- 30 combination of micrometer and nanometer sized.

The material may optionally comprise vertical cracks. The vertical cracks may vary in length from about 0.8 to about 1.0 times the thickness of the material. The vertical cracks generally are spaced at a distance less than the material thickness although in some applications, such as thermal barrier coatings, spacing up to about two times the thickness of the material may be useful. Vertical is herein defined as forming an angle of about 60° to about 120° with the material surface. Preferably the crack forms about a 90° angle with the material surface. The solution spray process may be manipulated to vary the amount and spacing of the cracks in the material through variations in the liquid injection position, primary plasma gas flow, and substrate temperature before and during spraying. In general the distance between the liquid injection nozzle and where the flame exits the flame nozzle can be determined without undue experimentation for the desired amount of cracking and crack spacing. When the primary plasma gas flow is high the material exhibits more cracking. High substrate temperatures tend to produce materials with higher levels of cracking.

The solution plasma spray process can be used to make materials having a unique structural morphology featuring fine splats, micrometer sized cracks perpendicular to the substrate surface (i.e., vertical cracks), and three-dimensional porosity.

The materials produce by the solution plasma spray method can include, for example, wear resistant coatings, corrosion resistance coatings, thermal barrier coatings, dielectric coatings, catalytic films, electrolyte layers, electrode layers, thick metal oxide coatings, solid conductive layers, soft magnetic films, semi-conductor films, sensors and activators and the like. In addition to coatings, the solution plasma spray method may be used to form preforms, layered materials, and composite materials containing nanoparticles and/or nanofibers for thermal insulation, wear and corrosion resistance, and solid state conductivity in the power generation, aerospace and fuel cell areas. Other potential applications include biomedical prostheses, advanced catalysis, battery electrodes, chemical sensors and physical sensors.

In one embodiment, the material comprises metal oxides, metal carbides, metal nitrides, metal silicides and combinations of the foregoing, wherein the metal

- is, for example, aluminum, boron, sodium, potassium, lithium, calcium, barium, and magnesium; transition metals such as chromium, iron, nickel, zinc, niobium, titanium, zirconium, scandium, yttrium, lanthanum, cerium, praseodymium, neodymium, samarium, terbium, ytterbium; and combinations comprising of the foregoing metals.
- 5 Stabilized or partially stabilized ceramics such as those stabilized by the presence of a rare earth-based compound may be used. Stabilized ceramics include, for example, zirconia stabilized with yttria (YSZ) or zirconia stabilized by ceria, scandia, calcia, magnesia, gadolinia, or lanthia.

- Preferred materials comprise single oxide ceramics such as Al_2O_3 (aluminum oxide) and NiO (nickel oxide), and mixed oxide ceramics such as Y_2O_3 -stabilized ZrO_2 (yttria-stabilized zirconia, or YSZ) and La_2O_3 doped CeO_2 (lanthia-doped ceria), composites such as $\text{NiZnFe}_2\text{O}_4$ and yttrium aluminum gadolinium (YAG).
- 10

- Particular embodiments include, for example, thermal barrier coatings such as ZrO_2 +7 percent by weight (wt%) Y_2O_3 based on the total weight of the material
- 15 (7YSZ), electrolyte layers such as ZrO_2 +20 wt% Y_2O_3 based on the total weight of the material (20YSZ), thick metal oxide coatings such as Al_2O_3 , anode layers such as NiO and La_2O_3 -doped CeO_2 (LDC), solid conductive layers such as La_2O_3 -doped CeO_2 , solid oxide fuel cell layers, and soft magnetic thick films such as NiZn -ferrite.

- The thickness and porosity of the material, as well as the presence or absence of cracking, will depend upon the form, type and composition of coating. All porosity
- 20 volume percents are based on the total volume of the coating. In the case of thermal barrier coatings, it is preferred that the coatings have a thickness of greater than about 125 micrometers and porosity of about 15 to about 40 volume%. For electrolyte layers, the thickness is preferably less than about 100 micrometers and porosity less
- 25 than about 5 volume%. A thick metal oxide coating can have a thickness of about 250-2500 micrometers and a porosity of about 20-40 volume%. Anode layers can have thicknesses of about 100 to about 200 micrometers with porosity of about 20 to about 50 volume%.

- In a bulk material or article fabrication process, the substrates can comprise
- 30 component templates of various geometries. After solution plasma spray deposition

of the material, the template can be removed, or alternatively, can be part of the formed article.

One embodiment is a Y_2O_3 -stabilized ZrO_2 (YSZ) thermal barrier coating (TBC) having the unique microstructural features illustrated in Figure 1C. Figure 1 is a schematic illustrating substrates 12 with conventional powdered feedstock plasma sprayed coating 11 (1A), an EB-PVD-deposited coating 13 (1B), and a solution plasma spray-deposited coating 14 (1C). The microstructural features of the solution plasma spray-deposited coating 14 include fine splats, vertical cracks 17, three-dimensional micrometer size porosity 16 and nanometer size porosity 15. The vertical cracking in the solution plasma spray-deposited coating can provide relief from thermal stress. The existence of micrometer size porosity and nanometer size porosity (i.e., duplex porosity) in the solution plasma spray-deposited coating can result in reduced thermal conductivity and thereby better thermal insulation properties as well as better thermal stress tolerance. The fine splats in the solution plasma spray-deposited coatings can increase coating integrity and decrease unfavorable cracking (especially lateral cracking) compared to a conventionally sprayed coating 13 that has a lamellar structure consisting of many large (i.e., 100 micrometers or greater) inherent splat boundaries as shown in Figure 3B. The unique coating structure is clearly exhibited in the scanning electron microscope (SEM) cross-sections in Figures 2A and 2B.

Other characteristics also are identified in the solution plasma spray deposited materials. The solution plasma spray deposited coatings typically consist essentially of nanometer sized features (<100 nanometers) comprising about 10 nanometers to about 5 nanometer size grains. The deposited materials are predominately nanostructured. Additionally the materials typically exhibit greater than about 90% crystallization, preferably greater than about 95% crystallization and more preferably greater than about 98% crystallization. Figure 3 shows a schematic of the microstructure of the coating illustrating the grain sizes. In the case of 7YSZ, the phase composition is primarily tetragonal- ZrO_2 and minor cubic- ZrO_2 rich with Y_2O_3 . The fractured surface of a 20YSZ coating prepared by the solution plasma spray process is shown in Figure 4.

As described above, the characteristics of the materials deposited by solution thermal spray can be systematically varied. The solution plasma spray process is flexible in producing materials with a porosity of about 1 to about 50 volume% of the total volume of the material. In Figure 5A, a dense 20YSZ coating with a porosity less than 2 volume% of the total volume of the coating is shown. In Figure 5B, a porous lanthanum doped-ceria ("LDC40") with nickel oxide ("NiO") coating with a porosity more than 40 volume% of the total volume of the coating is shown.

The combination of fine splats, vertical cracks and three dimensional porosity is especially valuable in thermal barrier coatings. As shown in Figure 9, yttria stabilized zirconia thermal barrier coatings deposited by solution plasma spray have improved durability in a thermal cycling test. The yttria-stabilized zirconia coatings can withstand about 1018 or more thermal cycles compared to less than 675 cycles for an EB-PVD coating and less than 391 cycles for plasma sprayed coatings employing a powdered feedstock. Each thermal cycle includes heating to 1121°C for 50 minutes followed by cooling for 10 minutes. A sample is considered to have failed when the area of spallation (i.e., where the coating is fully detached from the substrate) and delamination (i.e., where a portion of the coating is detached but still hanging from the substrate) reaches about 50% of the total area of the thermal barrier coating. Thus, a coating that can withstand 1018 cycles has an area of spallation and delamination of less than about 50% of the total area after 1018 cycles.

The thermal barrier coatings produced by solution plasma spray exhibit improved thermal cycling behavior even at coating thicknesses over 12 mils (305 micrometers). (Figure 10) Typically, the thicker the coating, the fewer cycles it can withstand. A 305 micrometer thick powdered feedstock plasma sprayed 7YSZ coating can withstand 391 thermal cycles, while a 305 micrometer solution plasma spray deposited 7YSZ coating can withstand 1018 cycles. Further, 508 micrometer and 635 micrometer solution plasma spray deposited coatings can withstand over 650 thermal cycles. Even a 1016 micrometer solution plasma spray deposited coating can withstand 555 thermal cycles.

The solution plasma spray deposited thermal barrier coatings exhibit improved thermal cycling behavior even when deposited on low roughness substrates (Figure 11). Both powdered feedstock plasma sprayed controls and solution plasma spray deposited 7YSZ coatings can withstand about 150 thermal cycles when deposited on a lightly blasted CMSX-4 superalloy single crystal with 75 % Pt-Al bond coat. The substrate had a roughness of about 1.1 micrometers. When deposited on a similar howmet substrate as received (i.e., having a roughness of about 5.5 micrometers), the powdered feedstock plasma sprayed control spalled, i.e., did not adhere to the substrate. The solution plasma spray deposited coating, however, withstood 180 cycles at 1151°C and 234 cycles at 1121°C. When deposited on a Solar substrate (CMSX-4 with a NiCrAl bond coat) with a roughness of about 25 micrometers, the powdered feedstock plasma sprayed control withstood 391 cycles, while the solution plasma spray deposited coating withstood 1018 cycles. Thus, the solution plasma spray deposited coatings displayed improved thermal cycling behavior as compared to powder feedstock plasma sprayed coatings on substrates of roughness varying from about 5 to about 25 micrometers.

The solution plasma spray deposited coatings 26 have about the same thermal conductivity (Figure 12) compared to those formed in conventional thermal spraying 25 and lower than that of coatings deposited by electron beam physical vapor deposition 24 process. The thermal conductivity of the deposited material can be varied by varying the porosity of the material.

With the solution plasma spray method, materials can be applied to various substrates made of metal, alloy, ceramic, and the like. The materials produced by the solution plasma spray method can include, for example, thermal barrier coatings; electrical and thermal insulating coatings; thick and thin coatings formed on steel, stainless, Mo, superalloy and ceramic substrates; wear resistant oxide coatings; solid reaction barriers (conductive layers) used for solid oxide fuel cells (SOFCs); electrolyte layers for SOFCs; anode layers for SOFCs; electrolyte layers for gas separation and purification of hydrogen from syngas in IGCC; and soft magnetic films for microwave radar and transducer devices. The materials can be used, for example, in applications requiring wear and corrosion resistance such as engines, dielectric and

thermal insulation, electrodes and electrolytes for solid oxide fuel cells, and in catalyst applications.

In one embodiment, the coatings can be used as electrolyte layers, conductive layers and/or electrode layers in solid oxide fuel cells (SOFCs). A fuel cell is a device in which a first reactant, a fuel such as hydrogen or a hydrocarbon, is electrochemically reacted with a second reactant, an oxidant such as air or oxygen, to produce a DC electrical output. A fuel cell includes an anode, or fuel electrode, a cathode, or oxidant electrode, and an electrolyte. In an SOFC, a solid electrolyte separates a porous anode from a porous cathode. The SOFC may also contain additional conductive layers or interconnects. Each individual fuel cell, made of a single anode, a single electrolyte, and a single cathode, generates a relatively small voltage, typically about 1 volt. To achieve higher voltages that are practically useful, the individual fuel cells are connected together in series to form a stack.

In the SOFC, the electrolyte layer is preferably dense and preferably has a thickness less than or equal to about 20 micrometers and a porosity less than or equal to about 5%. The anode layer of the SOFC porous and preferably has a thickness of about 2 micrometers for anode supported SOFCs or about 100-200 micrometers for cathode supported SOFCs and a porosity of about 20-40%. The cathode layer of the SOFC is preferably strontium doped LaMnO_3 and preferably has a thickness of 50 micrometers for anode supported SOFCs or 2 millimeters for cathode supported SOFCs and a porosity of about 40%. The reaction barrier is dense and preferably has a thickness of about 10-50 micrometers and a porosity of less than or equal to about 5%.

The invention is further illustrated by the following non-limiting examples.

25 EXAMPLES

Solution plasma spray was used to produce eight different coatings. In each of the coatings, a precursor solution was formed, poured into a 2-liter container and fed into the injector by a mechanical pump or a gas-pressure pump operating at 20 psig. The flow rate was regulated at about 20 to about 100 milliliters/minute by a flow

meter (Gilmont, Inc.). A fog nozzle was used to generate atomized droplets with nitrogen as an atomizing gas at 10-30 pounds per square inch (psi). The precursor solution was fed into the plasma in an external injection manner. In all cases, the precursor chemicals were reagent grade.

- 5 Unless otherwise noted, stainless steel was employed as the substrate. The substrate was coarsened by sand blasting (Al_2O_3 grit, 30 mesh), degreased and cleansed in acetone, and then preheated by plasma torch scanning. A Metco 9M plasma spray system was employed to deposit the coating. The system consisted of a 9MC plasma control console, a 9MCD distribution, a 9MR power supply unit and a
- 10 9MB direct current plasma gun. The gun was mounted on a six-axis robotic arm (GMFanuc S-700) and the substrate was attached to a turntable. The coating rate was about 5 to about 10 micrometers per pass at a deposition efficiency of about 30-60%. The spray parameters for the different coatings are summarized in Table 2. Primary and secondary gas flow are measured in standard cubic feet per hour (SCFH). Except
- 15 for Example 2, the primary plasma gas was argon at a pressure of 100 psi and the secondary plasma gas was hydrogen at a pressure of 50 psi. In Example 2 the primary plasma gas was argon at a pressure of 100 psi and the secondary plasma gas was helium at 50 psi. The plasma current is described in amperes. The plasma voltage is described in volts. The gun traverse speed and vertical speed is described
- 20 in millimeters per second (mm/s). The turntable speed is described in rotations per minute (rpm). The distance between the flame nozzle tip and the substrate (spray distance) is described in inches. The substrate preheat temperature is described in degrees Celsius.

Table 2- Spray parameters for solution thermal spray-deposited coatings

Example	1	2	3	4	5	6	7a	7b	8
Primary Gas flow rate (SCFH)	140	80	120	160	120	160	120	160	80
Secondary Gas flow rate (SCFH)	20	15	20	23	20	23	20	23	15
Plasma Current (amp)	650	650	650	600	650	600	650	600	650
Plasma voltage (volts)	65	70	70	65	70	65	70	65	70
Anode nozzle type	GP	GE	GP	GH	GP	GH	GP	GH	GP
Gun traverse speed (mm/s)	1000	500	50	100	100 s	100	100	100	1000
Gun vertical speed (mm/s)	4	2	-	-	-	-	-	-	-
Turntable speed (rpm)	-	-	60	430	430	430	430	430	4
Spray distance (in)	2	2	1.5	3	2.5	3	2.5	3	2
Substrate preheat temperature (°C)	350	350	200	200	300	200	200	200	300

Example 1: $\text{ZrO}_2+7 \text{ wt}\% \text{Y}_2\text{O}_3$ (7YSZ) Thermal Barrier Coating

5 The precursor solution was formed as follows. Zirconium salt was dissolved in a weak organic acid and then mixed with distilled water to form a solution containing 22 wt% zirconium acetate at a pH of 3-5. 1000 grams of the Zr solution was mixed with 56.7 grams yttrium nitrate to form a precursor solution. The coating was formed by deposition of the precursor solution according to the parameters in Table 2.

10 The solution plasma spray deposited 7YSZ had a porosity of about 15 volume% to about 30 volume% of the total volume of the coating and a thickness of

about 300 micrometers to about 500 micrometers. The 7YSZ coating was well bonded to the substrate, contained fine splats, and contained some spaced vertical cracks as well as micrometer and nanometer-sized porosity. Figure 2 shows the splats and vertical cracking. Moreover, the 7YSZ coating structure was verified to be stable
5 in retaining nanometer grain size and reducing sintering during long-term exposure at an elevated temperature of 1121°C.

Using the above procedures, bond coated (MCrAlY) Ni-based superalloy substrates were used for deposition of YSZ ceramic coatings. The deposited coatings were subjected to physical, microstructural and performance evaluation.

10 Example 2: $\text{ZrO}_2 + 20 \text{ wt } \% \text{Y}_2\text{O}_3$ (20YSZ) Electrolyte Layer

The precursor solution was formed by dissolving zirconium acetate in acetic acid and then mixing with distilled water to form a solution containing 22 wt% zirconium acetate with a pH of 3.5. Then 222 grams of yttrium nitrate were mixed with 1000 grams of the solution to form the precursor solution. The coating was
15 formed by deposition of the precursor solution according to the parameters in Table 2.

The solution plasma spray deposited 20YSZ had a porosity of less than about 2 volume% of the total volume of the coating (Figure 7A). The coating was crack-free and adherent to the substrate when its thickness was below 100 micrometers. However, vertical cracks and coating exfoliation occurred in coatings having a
20 thickness more than 200 micrometers. The coating comprised cubic- ZrO_2 .

A stainless steel strip was coated with a solution plasma spray-applied 20YSZ coating, then bent into 90° angles. As shown in Figure 13, no spallation in the deformed area was found with the exception of minor cracks and slightly peeling of the coating at the edge area.

25 Example 3: Al_2O_3 Coating

The precursor solution was prepared by dissolving aluminum nitrate in distilled water to form a 1.0 mole precursor solution. The coating was formed by deposition of the precursor solution according to the parameters in Table 2.

Example 4: NiO Anode Layer for an SOFC Unit

A sintered LaSrMn oxide tube (1.22 inches in outer diameter) was coated with NiO oxide using the solution plasma spray method. The precursor solution was prepared by dissolving 484 grams of nickel nitrate, i.e. $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, in distilled water to form a solution. The coating was formed by deposition of the precursor solution according to the parameters in Table 2.

The solution plasma spray deposited NiO had a porosity of about 35 to about 45 volume% of the total volume of the coating (Fig. 7B) and a thickness of about 100 to about 200 micrometers. The coating microstructure was characterized by aggregated fine particles, weak cohesion and adherence to the substrate.

Example 5: La_2O_3 -doped CeO_2 Solid Conductive Layer

A sintered strontium doped LaMnO_3 oxide tube (1.22 inches in outer diameter, provided by Siemens Westinghouse Power Corp.) was used as a substrate for the fabrication of a La_2O_3 -doped CeO_2 ("LDC40") coating using the solution plasma spray method. The precursor solution was prepared by dissolving 73.8 grams cerium acetate $\text{Ce}(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot 1.5\text{H}_2\text{O}$ and 49 grams lanthanum acetate $\text{La}(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot 1.5\text{H}_2\text{O}$ in distilled water to form a 1.0 liter precursor solution. The coating was formed by deposition of the precursor solution according to the parameters in Table 2.

The LDC40 layer with a thickness of about 10 micrometers fully covered the tube surface.

Example 6: LDC40+NiO Anode Layer

A sintered strontium doped LaMnO_3 oxide tube (1.22 inches in outer diameter, provided by Siemens Westinghouse Power Corp.) was used as a substrate for the formation of a mixed LDC40+NiO layer using the solution plasma spray method. The precursor solution was prepared by dissolving 484 grams of nickel nitrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 73.8 grams cerium acetate $\text{Ce}(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot 1.5\text{H}_2\text{O}$ and 49 grams lanthanum acetate $\text{La}(\text{C}_2\text{H}_3\text{O}_2)_3 \cdot 1.5\text{H}_2\text{O}$ in distilled water to form a 1.0 liter precursor

solution. The coating was formed by deposition of the precursor solution according to the parameters in Table 2.

The solution plasma spray deposited LDC+NiO had a porosity of about 35 to about 45 volume% of the total volume of the coating and a thickness of about 100 to about 200 micrometers. The coating microstructure was characterized by aggregated fine particles, weak cohesion, and adhesion to the substrate. The LDC+NiO phase composition was analyzed by X-ray diffraction analysis. The analysis indicated the presence of LDC and NiO phases with near complete crystallization in the as-deposited layer, shown in Figure 14.

10 Example 7: LSM Tube/LSGM/LDC/LDC+NiO Solid Oxide Fuel Cell (SOFC) Unit

A single solid oxide fuel cell was fabricated by sequential thermal spraying a LaSrGaMn electrolyte, a LDC40 barrier and an LDC40+NiO anode on a sintered LaSrMn oxide tube substrate as cathode. First, a $\text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}$ oxide (Praxair Specialty Ceramics) electrolyte layer was deposited onto the tube by conventional powdered feedstock plasma spray. Next, an LDC40 barrier was applied by the solution plasma spray process (coating 7a) as described in Example 5. Last, an LDC40+NiO anode layer was deposited using the solution plasma spray process (coating 7b) as described in Example 6.

A single SOFC fabricated by the solution plasma spray process was examined in cross-section by SEM observation. Figure 15 illustrates that the solution plasma spray-LDC+NiO anode layer and the solution plasma spray-LDC barrier layer satisfy the SOFC's requirements for a high porosity, thin coating.

Example 8: NiZn-Ferrite Soft Magnetic Thick Film

A $\text{Ni}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ thick film was deposited on aluminum substrate using the solution plasma spray method. The precursor solution was prepared by dissolving 101 grams iron nitrate $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, 18 grams nickel nitrate $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, 18 grams zinc nitrate $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in distilled water to form a 1.0 liter precursor solution. The solution pH value was adjusted to 3.0 by adding appropriate amount of

ammonium hydroxide. The coating was formed by deposition of the precursor solution according to the parameters in Table 2.

The NiZn-ferrite film had high purity, good stoichiometry and crystallinity confirmed by magnetic property measurement and X-ray diffraction analysis. The film was uniform in thickness and composition. The saturation magnetization of as-deposited NiZn-ferrite was near 90 percent of bulk material with the same composition.

Example 9: Varying the morphology of a 20YSZ coating

The 20YSZ coating was produced using precursor solutions as in Example 2. Coatings were produced under three conditions: 1. low plasma heat input and substrate temperature, 2. high plasma heat input and substrate temperature, and 3. moderate plasma heat input and substrate temperature. Under condition 1, the coating produced had splats of about 5 to about 20 micrometers and nodules of less than 1 micrometer (Figure 16A). Under condition 2, the coating produced had fine splats (Figure 16B). Under condition 3, the coating produced had a combination of the morphologies produced by conditions 1 and 2 (Figure 16C).

Solution plasma spray has been employed to make coatings having a unique microstructure. The materials have fine splats, vertical cracks, and three-dimensional porosity. The microstructure of the materials makes them well suited for applications requiring exposure to temperatures of 1000°C or higher, strong interface strength, low thermal conductivity and/or stress tolerance. The materials have many uses such as thermal barrier coating for hot-section components in gas turbine engines for jet aircraft and power generation and the like. Other applications include use as dielectric coatings, catalytic films, doped oxide films for use in fuel cells and gas separation and purification, electronic and ionic conductivity membranes and sensor devices. Because of the unique structure of the materials, they may even be used to form ceramic engines for aircraft applications.

While the invention has been described with reference to a preferred embodiment, it will be understood by those skilled in the art that various changes may

be made and equivalents may be substituted for elements thereof without departing from the scope of the invention. In addition, many modifications may be made to adapt a particular situation or material to the teachings of the invention without departing from essential scope thereof. Therefore, it is intended that the invention not
5 be limited to the particular embodiment disclosed as the best mode contemplated for carrying out this invention, but that the invention will include all embodiments falling within the scope of the described embodiments.

All cited patents, patent applications, and other references are incorporated herein by reference in their entirety.

10

EMBODIMENTS:

5 A first embodiment is a method of producing a material comprising injection precursor solution droplets into a hot zone of a thermal spray flame, converting the precursor solution droplets into particles, at least partially melting the particles and depositing the particles on a substrate.

A second embodiment is a method of producing a material comprising injection precursor solution droplets into a hot zone of a thermal spray flame, converting the precursor solution droplets into particles, at least partially melting the particles and depositing the particles on a preheated substrate.

10 A third embodiment is a method of producing a material comprising injection precursor solution droplets into a hot zone of a thermal spray flame, converting the precursor solution droplets into particles, at least partially melting the particles and depositing the particles on a substrate wherein the temperature of the substrate is controlled during deposition of the particles.

15 A fourth embodiment is a material comprising splats having an average diameter of less than or equal to about 2 micrometers.

A fifth embodiment is a material comprising splats having an average diameter of less than or equal to about 2 micrometers and a thickness less than or equal to about 800 nanometers.

20 A sixth embodiment is a material comprising splats having an average diameter of less than or equal to about 2 micrometers and porosity of about 1 to about 50%.

25 A seventh embodiment is a material comprising splats having an average diameter of less than or equal to about 2 micrometers and three dimensional, interpenetrating porosity of about 8 to about 50%.

An eighth embodiment is a material comprising splats having an average diameter of less than or equal to about 2 micrometers and porosity of about 1 to about 50% comprising micrometer and/or nanometer sized pores.

- 5 A ninth embodiment is a material comprising splats having an average diameter of less than or equal to about 2 micrometers and vertical cracks.

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COATINGS, MATERIALS, ARTICLES, AND METHODS OF MAKING
THEREOF

ABSTRACT OF THE DISCLOSURE

- 5 A thermal spray process comprises injecting precursor solution droplets into the hot zone of the thermal spray flame. Also described are materials resulting from the process.

Fig.1

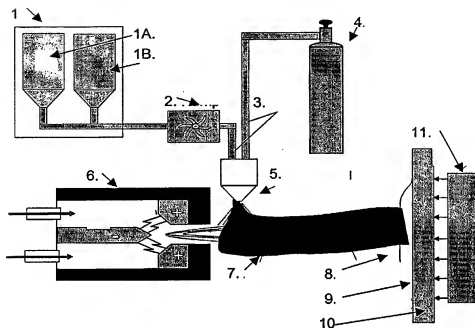
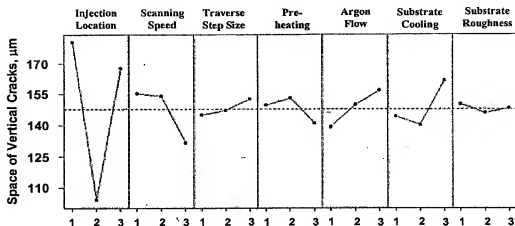


Fig. 2

A



B

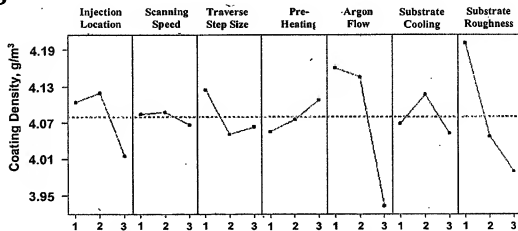


Fig. 3

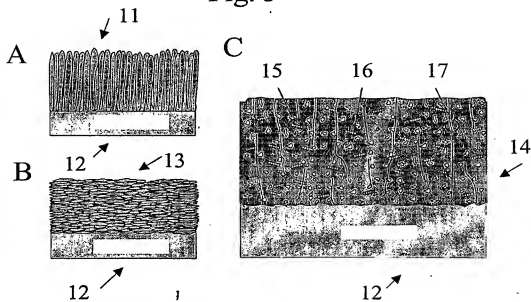


Fig. 4

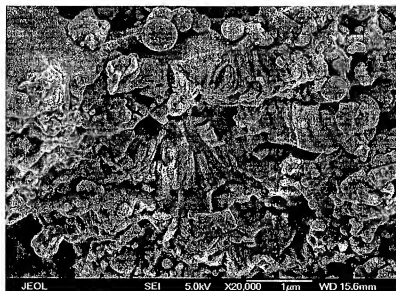


Fig. 5

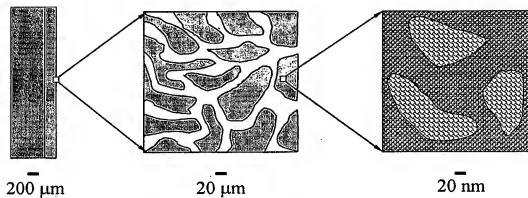


Fig. 6

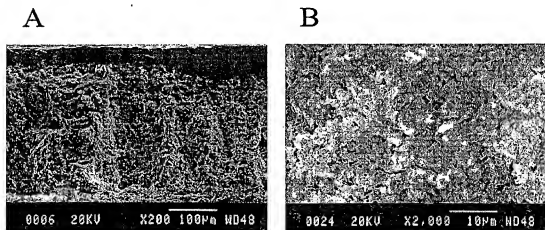


Fig. 7

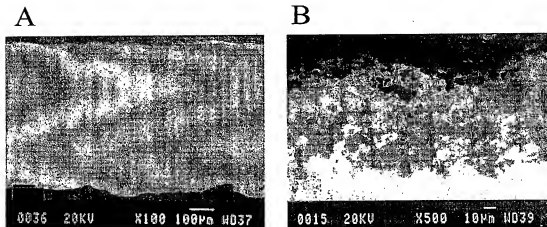


Fig. 8

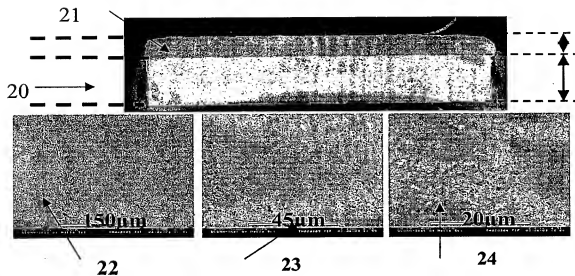


Fig. 9

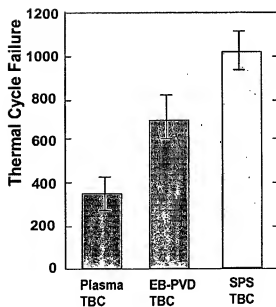


Fig. 10

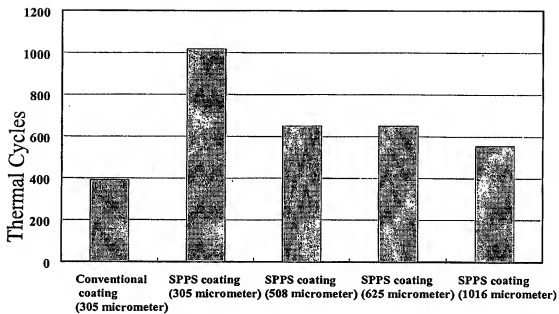


Fig. 11

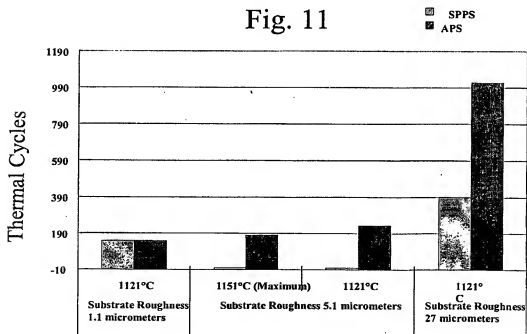


Fig. 12

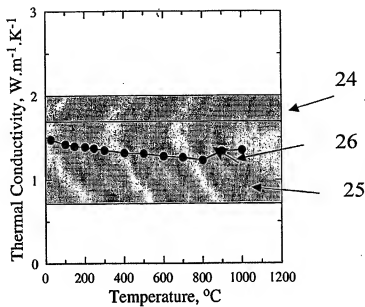


Fig. 13

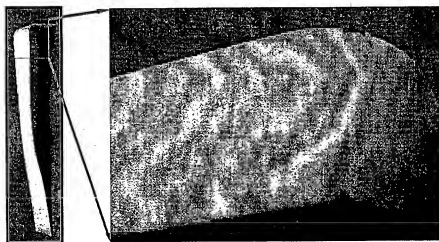


Fig. 14

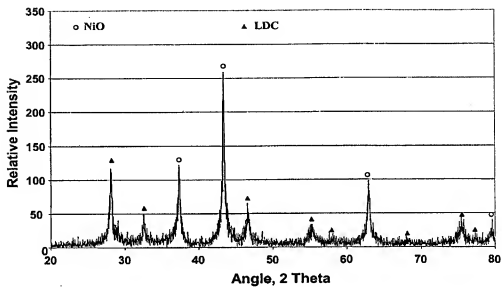


Fig. 15

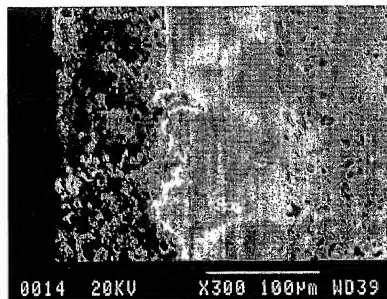


Fig. 16

